

# Dynamic heterogeneities in attractive colloids

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We study the formation of a colloidal gel by means of Molecular Dynamics simulations of a model for colloidal suspensions. A slowing down with gel-like features is observed at low temperatures and low volume fractions, due to the formation of persistent structures. We show that at low volume fraction the dynamic susceptibility, which describes dynamic heterogeneities, exhibits a large plateau, dominated by clusters of long living bonds. At higher volume fraction, where the effect of the crowding of the particles starts to be present, it crosses over towards a regime characterized by a peak. We introduce a suitable mean cluster size of clusters of monomers connected by “persistent” bonds which well describes the dynamic susceptibility.

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Recent advances in colloidal science allow to obtain colloidal particles or nanoparticles with specific functional properties, of electronic, chemical, biological or mechanical nature. Hence the packing and aggregation of colloidal particles are important for a wide variety of applications, including biological arrays, sensors, paints, ceramics, and photonic crystals.

In particular, by adding polymers to a colloidal solution, it is possible to induce an effective short range attraction between colloidal particles, known as depletion effect. Attractive colloids exhibit a rich phenomenology in the temperature - volume fraction plane [1, 2, 3, 4, 5, 6, 7]: At high temperature the attraction can be neglected and, by increasing the volume fraction, if crystallization is avoided, a hard sphere glass transition occurs. By decreasing the temperature, the effect of the short range attraction induces an attractive glass line which is strongly temperature dependent, as predicted by Mode Coupling Theory [8], and by mean field theory [9]. This line at low volume fraction is identified as a gelation line. In fact at low temperature and low volume fraction, attractive colloids are known to exhibit a structural arrest with properties similar to the sol-gel transition [3, 10, 11, 12, 13]. Although intensively studied both experimentally and numerically, the theoretical understanding of colloidal gelation, compared with chemical (irreversible) gelation and glass transition, is still far from being reached.

A promising approach to the comprehension of the complex dynamics of such systems is based on the study of the dynamical heterogeneities. This concept has been successfully introduced in glasses [14, 15, 16, 17, 18, 19, 20], to take into account the correlated motion of particle clusters, which decorrelates after a characteristic time  $\tau$ , of the order of the relaxation time. These dynamic heterogeneities are described quantitatively via

the so-called dynamic susceptibility [16]. In a Lennard-Jones binary mixture, a typical model for glass transition [21], the dynamic susceptibility grows as a function of the time, reaches a maximum and then decreases to a constant [20], consistently with the transient nature of the dynamic heterogeneities. Dynamic heterogeneities have been also observed in attractive colloidal systems in both experiments [23, 24] and numerical simulations [25, 26, 27]. In particular in [27] a systematic study of the dynamic susceptibility was done along the attractive glassy line. Typically the dynamic susceptibility displays a well pronounced peak, however in the attraction-dominated limit, the dependence on both time and wave vector markedly differs from that in standard repulsion-dominated systems (hard-sphere limit).

A rather different behavior was instead found recently in a model for irreversible gels, made of monomers with permanent bonds [22]. It was shown in fact that the dynamic susceptibility, defined as the fluctuations of the self Intermediate Scattering Function (ISF) [19], in the limit of low wave vector,  $k \rightarrow 0$ , tends for long times to a plateau, whose value coincides with the mean cluster size. As a consequence, as the system approaches the gel transition (i.e. the percolation threshold), the value of the plateau diverges. Such finding shows that, in irreversible gelation, the heterogeneities coincide with clusters of monomers linked by permanent bonds, and differently from glasses, have a static origin and do not exhibit any decay.

In this paper we study the dynamic susceptibility in a DLVO type of model for colloidal gelation [28, 29], at very low volume fraction and temperature, where the system exhibits more markedly gelation properties. Using MD simulations we find an interesting and completely unusual behavior. The dynamic susceptibility, for low wave vectors, increases with time until it reaches a large

plateau value of the order of the mean cluster size, as found in the model for irreversible gels, and for time larger than the bond lifetime, it decays to 1. Only at higher volume fractions, where the bond lifetime is comparable to the density-density structural relaxation time, the dynamic susceptibility exhibits a crossover towards the glassy behaviour with a well pronounced peak. Interestingly, a proper definition of a time dependent mean cluster size, where a cluster is made of “mobile” particles connected by bonds present at both time 0 and  $t$ , well reproduces the observed behavior of the dynamic susceptibility for a fixed low temperature and low volume fractions. At higher volume fraction, however, the dynamic susceptibility starts instead to display a peak and shows a discrepancy with the time dependent mean cluster size. This indicates a crossover towards a new regime where, besides the clusters, also the crowding of the particles starts to play a role in the slowing down of the dynamics. Although we have considered a DLVO type of model, we expect that the main results of our paper should be valid also for other model systems exhibiting colloidal gelation [30, 31].

*The model* - The DLVO model, considered here, has been previously studied using Molecular Dynamics (MD) [12, 13, 32]. In agreement with experimental findings [29], this model displays a structural arrest very close to the percolation threshold at low temperature, where clusters are made of particles connected by long living bonds [33].

In Refs. [32], we found that, at low temperatures, increasing the volume fraction, the system undergoes a transition from a disordered cluster phase to an ordered hexagonal lattice of tubular structures and, at higher volume fraction, to an ordered lamellar phase. If this ordered state is avoided, the system enters a “supercooled” metastable liquid phase until structural arrest (gel) occurs [12, 34] very close to the percolation threshold. For this reason we introduce here a small degree of polydispersity, which actually hinders the formation of the ordered phases. In this way we are able to fully investigate and characterize the gel formation at different temperatures and volume fractions. The interaction potential between two particles  $i$  and  $j$  is:

$$V_{ij}(r) = \epsilon \left[ A \left( \frac{\sigma_{ij}}{r} \right)^{36} - B \left( \frac{\sigma_{ij}}{r} \right)^6 + C \frac{e^{-r/\xi}}{r/\xi} \right] \quad (1)$$

where  $A = 3.56$ ,  $B = 7.67$ ,  $C = 75.08$ ,  $\xi = 0.49$  [35], and  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ . In the following we consider the radii  $\sigma_i$  randomly distributed in the interval  $\sigma - \delta/2 < \sigma_i < \sigma + \delta/2$  with  $\delta = 0.05\sigma$ . The potential is truncated and shifted to zero at a distance of  $3.5\sigma$ . The temperature  $T$  is in units of  $\epsilon/k_B$ , where  $k_B$  is the Boltzmann constant, wavevectors are in units of  $\sigma^{-1}$ , and times in units of  $\sqrt{m\sigma^2/\epsilon}$ , where  $m$  is the mass of the particles. The volume of the simulation box is kept constant,  $V = 5000\pi\sigma^3/3$ , and different volume fractions are

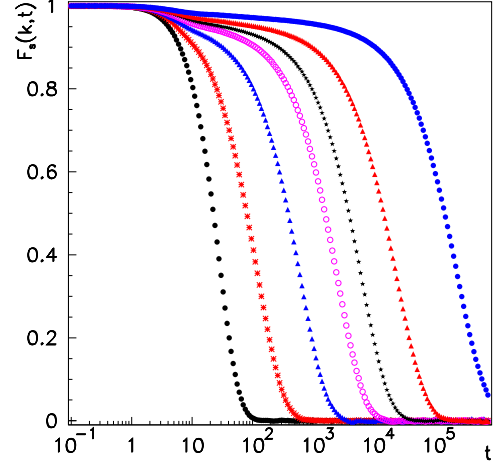


FIG. 1: (color online). The self ISF,  $F_s(k, t)$ , for  $T = 0.15$ ,  $k_{min} = 2\pi/L \simeq 0.36$ , and  $\phi = 0.01, 0.05, 0.08, 0.10, 0.11, 0.12, 0.13$  (from left to right).

obtained by varying the number of particles  $N$ , so that  $\phi = \pi\sigma^3 N/6L^3$ . We have performed Newtonian MD at constant NVT using the velocity Verlet algorithm and the Nosé-Hoover thermostat with time step  $\Delta t = 0.01$ .

At low temperatures and low volume fractions, we find the same properties as in the monodisperse case [12]: A cluster phase followed by a percolation transition in the same universality class as random percolation.

*Self Intermediate Scattering Function*- In order to study the dynamic behaviour of the model, we measure the self ISF,  $F_s(k, t) = \frac{1}{N} \langle \Phi_s(k, t) \rangle$ , where  $\Phi_s(k, t) = \sum_{i=1}^N e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_i(0))}$ ,  $\langle \dots \rangle$  is the thermal average, and  $\vec{r}_i(t)$  is the position of the  $i$ -th particle at the time  $t$ . In Fig. 1  $F_s(k, t)$  is plotted for  $T = 0.15$  and wave vector  $k_{min} = 2\pi/L \simeq 0.36$ . Increasing the volume fraction, the relaxation functions show a two-step decay, with a plateau value decreasing with the wave vector; The long time tail is fitted by stretched exponentials.

From the self ISF we calculate the structural relaxation time,  $\tau_\alpha(k)$ , defined as  $F_s(k, \tau_\alpha(k)) \simeq 0.1$ . In Fig. 2  $\tau_\alpha(k_{min})$  is plotted as a function of the volume fraction for two values of temperature,  $T = 0.15$  and  $0.25$ . In the same figure for the sake of comparison we also plot the bond lifetime,  $\tau_b$  [36], defined through the bond correlation function as  $B(\tau_b) \simeq 0.1$ , where  $B(t) = \frac{\sum_{ij} [\langle n_{ij}(t)n_{ij}(0) \rangle - \langle n_{ij} \rangle^2]}{\sum_{ij} [\langle n_{ij} \rangle - \langle n_{ij} \rangle^2]}$ ,  $n_{ij}(t) = 1$  if particles  $i$  and  $j$  are bonded at time  $t$ ,  $n_{ij}(t) = 0$  otherwise [33]. The data show that, at the lower temperature,  $T = 0.15$ , and at low volume fractions, where the bond lifetime is larger than the structural relaxation time,  $\tau_\alpha(k_{min})$  can be fitted by a power law,  $(\phi_c - \phi)^{-a}$ . In this regime the system dynamically behaves as if made of permanent clusters as

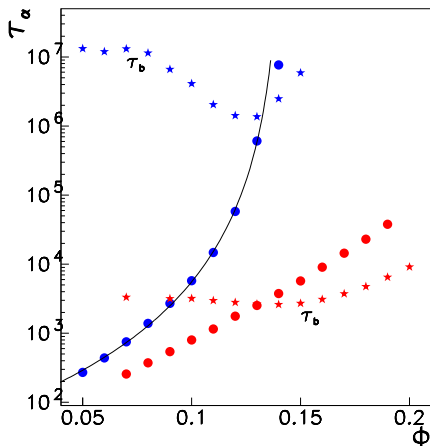


FIG. 2: (color online). The structural relaxation time,  $\tau_\alpha(k_{min})$  (circles), compared with the bond relaxation time,  $\tau_b$  (stars), for  $T = 0.15$  and  $0.25$  (from bottom to top). The continuous line is a power law fit  $(0.14 - \phi)^{-3.8}$ .

in irreversible gels. At the higher temperature,  $T = 0.25$ , instead the bond lifetime is of the same order of magnitude than the structural relaxation time, and we observe a smooth increase of  $\tau_\alpha(k_{min})$  not associated to a power law critical behavior.

*Dynamic heterogeneities* - According to the above interpretation of the dynamics, we should expect, for time windows comparable or larger than  $\tau_b$ , a deviation from the dynamics of irreversible gels even for  $T = 0.15$ . This crossover in the dynamics can be better stressed by looking at the dynamic susceptibility, defined as  $\chi_4(k, t) = \frac{1}{N} [|\Phi_s(k, t)|^2 - |\langle \Phi_s(k, t) \rangle|^2]$ .

In the main frame of Fig. 3,  $\chi_4(k_{min}, t)$ , is plotted as function of  $t$ , for  $T = 0.15$  and different  $\phi$ . For low volume fractions, after a time roughly of the order  $\tau_\alpha$ ,  $\chi_4(k_{min}, t)$  reaches a plateau, close to the value of the mean cluster size,  $S = \sum_s s^2 n_s / \sum_s n_s$  (see also the inset of Fig. 3 where the maximum of the dynamic susceptibility is compared with the mean cluster size), and decays after a time roughly of the order  $\tau_b$ . Only for times much smaller than  $\tau_b$  the system behaves as if the bonds were permanent. As the volume fraction increases,  $\tau_b$  and  $\tau_\alpha$  become of the same order of magnitude, the plateau disappears and  $\chi_4(k_{min}, t)$  exhibits a sharp peak similar to those of glassy systems. We have also checked that for temperature  $T = 0.25$ ,  $\chi_4(k_{min}, t)$  exhibits a small peak and no plateau.

The long time behaviour of  $\chi_4(k_{min}, t)$  can be quantitatively described in terms of a time dependent mean cluster size,  $S(t)$ . The function  $S(t)$  is the mean cluster size defined by persistent bonds, that is bonds that are

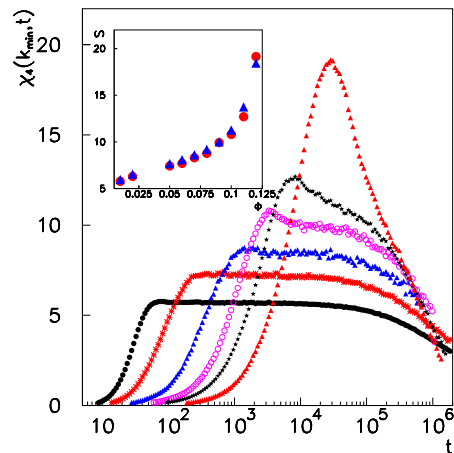


FIG. 3: (color online). **Main frame:** The fluctuations of the self ISF,  $\chi_4(k_{min}, t)$ , for  $T = 0.15$  and  $\phi = 0.01, 0.05, 0.08, 0.10, 0.11, 0.12$  (from left to right). **Inset:** The mean cluster size,  $S$  (triangles), as a function of the volume fraction,  $\phi$ , compared with the maximum of the dynamic susceptibility,  $\chi_4(k_{min}, t^*)$  (circles).

present at both time 0 and time  $t$  [37] (see inset of Fig. 4). To describe also the short time behaviour of  $\chi_4(k_{min}, t)$  we note that the main contribution to  $\chi_4(k_{min}, t)$  comes from the “mobile” particles [38]. We therefore modify further the definition of the mean cluster size introducing a mean cluster size for “mobile” particles,  $S_m(t)$ , where the clusters are made as before by particles connected by persistent bonds, but restricted to particles that in the time interval  $[0, t]$  have moved at least a distance  $r_0$ . For each volume fraction, we fix  $r_0$  so that the time at which  $S_m(t)$  and  $\chi_4(k_{min}, t)$  start to grow is the same. We find that  $r_0$  depends on the volume fraction roughly as  $\phi^{-1/3}$ . In main frame of Fig. 4,  $S_m(t)$  is compared with  $\chi_4(k_{min}, t)$ . At least at very low volume fractions, the two quantities agree surprisingly well. At  $\phi = 0.10$  a deviation begins to appear, that becomes manifest at  $\phi = 0.12$ , in the shape of a peak that grows to values higher than  $S_m(t)$  or  $S(t)$ . This peak, which appears when  $\tau_\alpha$  and  $\tau_b$  are of the same order of magnitude shows that the contribution to dynamic correlations, comes not only from the presence of long living clusters but also from the crowding of the particles.

In conclusions we have shown that in a model for colloidal systems at low volume fraction when the bond lifetime is much smaller than the relaxation time, the dynamic heterogeneities can be described in terms of time dependent clusters made of “persistent” bonds. We suggest that the analysis presented here should apply not only to colloidal gelation at low volume fraction, but also to micellar system, where a crossover from gel-like to glass-like behavior was found experimentally and nu-

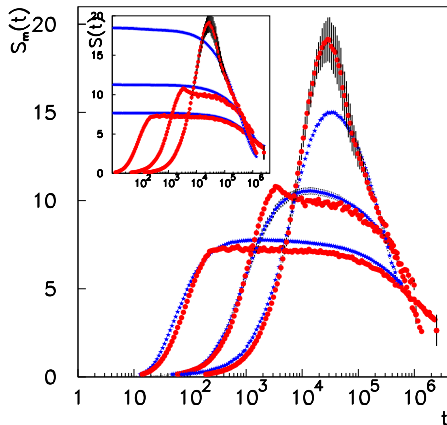


FIG. 4: (color online). **Main frame:** The dynamic susceptibility,  $\chi_4(k_{min}, t)$  (circles), compared with the time depending mean cluster size of mobile particles,  $S_m(t)$  (stars) for  $T = 0.15$  and  $\phi = 0.05, 0.10, 0.12$ . **Inset:**  $\chi_4(k_{min}, t)$  (circles) compared with the time depending mean cluster size,  $S(t)$  (stars) for the same temperature and volume fractions.

merically [41]. These findings offer a unique and coherent interpretation of dynamic heterogeneities in gelling systems. Finally, we also suggest that the concept of time dependent cluster, considered here, may be generalized to give a satisfactory definition of dynamic heterogeneities also for Lennard-Jones or hard sphere glasses.

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